Laboratory Name: Ames
B&R Code: KC-02-01-01

FWP and possible subtask under FWP:
Solidification Science

FWP Number:
AL-90-501-002

Program Scope:
Research effort is directed toward gaining an increased understanding of the fundamental behavior of crystal-melt interfaces and the associated dynamics that give rise to solidification microstructures in metallic materials. Development of the requisite theory involves descriptions of the physical interactions that operate at spatial and temporal scales ranging over several orders of magnitude, from the microstructural scale ($10^{-6} – 10^{-3}$m) down to the atomistic level ($10^{-8} – 10^{-10}$m).

Major Program Achievements (over duration of support):
- First reported quantitative experimental measurement of anisotropy in the crystal-melt interfacial free energy in Al-Cu and Al-Si binary alloys.
- Theoretical prediction of anisotropy for the free energy of the crystal-melt interface for pure aluminum.
- Theoretical solution for the full equilibrium morphology of a grain boundary groove at a solid liquid interface with generally anisotropic interfacial free energy.
- The theoretical basis was established for an oscillating interface approach to the measurement of interfacial mobility in pure metals and alloys.
- Theoretical modeling of complex fluid flow in directional solidification and its interaction with the solidifying interface, that gives rise to oscillatory two-phase structures in peritectic systems.
- Development of a "thin-sample" experimental technique for the suppression of convective flow during directional solidification, enabling isolation and investigation of diffusive growth mechanisms.
- Validation of a theoretical model for diffusive band formation in two different alloy systems.
- Utilization of the theoretical banding cycles in Sn-Cd and Pb-Bi for the experimental determination of nucleation undercoolings for the primary and "peritectic" phases. A nucleation map was developed for the two-phase system that identifies the experimental regimes for nucleation at (i) the S/L interface, (ii) the ampoule wall, or (iii) the interface-wall junction.

Program impact:
The thermodynamic and kinetic properties which originate at the atomistic or even electronic level ultimately govern the dynamics of morphological transitions, and a quantitative understanding of these properties is required for substantive theoretical advancement and the development of predictive capability. The approach taken in this focus area utilizes analytical, computational, and experimental tools, which lead to the advancement of solidification theory.

Interactions:
- Contribution to both theoretical and experimental efforts within scope of the Computational Materials Science Network (US DOE) project, Microstructural evolution based on fundamental interfacial properties, Tony Rollett, David Srolovitz, and Alain Karma, Principal Investigators
- In-situ diffraction studies at the Advanced Photon Source (Argonne National Laboratory) MU-CAT beamline, aimed at quantifying phase competition in peritectic alloys, i.e. Sn-Sb
- The DOE-BES sponsored Process Science Initiative was integral for the initial work on grain boundary grooves and measurement of interface energy anisotropy

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
R. K. Trivedi – Henry Marion Howe Medal from ASM International; Bruce Chalmers Award from TMS
5 invited talks since 2000

Principal Investigator Commitments for FY2002 to Nearest +/- 10%:
R.E. Napolitano [Coordinator] (50%), R.K. Trivedi (20%), S.B. Biner (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $191 k **FY01 BA $**236 k **FY02 BA $**644 k*

* The significant increase in funding was a result of an FY02 restructuring of the research efforts within the Program and the formation of a *Solidification Science* focus area..

Laboratory Name: Ames
B&R Code: KC-02-01-03

FWP and possible subtask under FWP:
Magnetism

FWP Number:
AL-90-501-004

Program Scope:
Research efforts are directed toward understanding the interplay between competing energy contributions in determining critical magnetic phenomena. Of particular interest are material systems containing magnetic rare earths, transition metals, or both, where characteristic structural dimensions are on the order of the magnetic interaction lengths, or the energy difference between crystalline states is of the same order as the energy difference between magnetic states. Systematic experimental and theoretical studies are designed to formulate and validate a consistent predictive theory describing, and therefore enabling the control of magnetic phenomena at various length scales. The experimental program is strongly linked to theory and modeling.

Major Program Achievements (over duration of support):
- Discovered two new magnetic phases in between 110 and 125 K in a magnetic field of 3 to 7 kOe and between 178 and 182 K in magnetic fields of 6 to 12 kOe.
- Theoretically derived and experimentally validated fundamental relationships between the characteriustic isothermal entropy and adiabatic temperature changes of the magnetocaloric effect (MCE) and heat capacity at constant pressure as a function of temperature in constant magnetic field.
- Showed that the "ferromagnetic" transition in the bulk metallic glass $Nd_{60}Fe_{30-x}Al_{10+x}$ is a frequency dependent spin glass transition.
- Derived an extension to the magnetomechanical law of approach for describing and modeling magnetoelastic effects.
- Developed a formalism has been developed to incorporate stress into the effective field of the Landau-Lifschitz-Gilbert equation as a perturbation to the anisotropy in order to allow micromagnetic modeling of stress dependent magnetization processes.

Program impact:
Provided insights on magnetic interactions and phenomena propagating over spatial scales from atomistic to macroscopic and temporal scales that vary over several orders of magnitude. Included are the significant interactions of magnetic and crystallographic phase transformations in both the magnetocaloric effect and magnetostriction.

Interactions:
In addition to the Condensed Mater Physics and Materials Chemistry Programs within Ames Laboratory, collaboration with other National Laboratories include: Argonne, Brookhaven, Idaho National Engineering and Environmental Laboratory, and the Naval Surface Weapons Center. Collaborations with US universities include: Iowa State University, MIT, Ohio State University, and the University of Maryland. International collaborations include: Facultad de Matematica Astronomia y Fisica (FaFAM), Ciudad Universitaria, Cordoba, Argentina; Hanoi National University/Hanoi; Institute of Physics of the Czech Academy of Sciences; Moscow State University, University of Quebec, and University of Rio De Janeiro.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
K.A. Gschneidner, Jr. – Honorary member of the European rare earth and Actinide Society (1998)
D.C. Jiles – Fellow of the American Physical Society (1997); Magnetics Society Distinguished Lecturer (1997-98)
R.W. McCallum – DoE Materials Sciences Award for Sustained Outstanding Research in Solid State Physics (1995)
V.K. Pecharsky – Editor of *Handbook on the Physics and Chemistry of Rare Earths*, 2001-present. Technical Editor of *Advances in Cryogenic Enginee*ring, 1999-present.
21 invited talks since 2000

Principal Investigator Commitments for FY2002 to Nearest +/- 10%:
R.W. McCallum [Coordinator] (40%), K.A. Gschneidner, Jr. (30%), V.K. Pecharsky (30%),
J.E. Snyder (30%), D.C. Jiles (10%), T.A. Lograsso (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA ~$700 k **FY01 BA** ~$750 k **FY02 BA $**1140 k*

* The significant increase in funding was a result of an FY02 restructuring of the research efforts within the Program and the formation of a *Magnetism* focus area..

Laboratory Name: Ames
B&R Code: KC-02-01-03

FWP and possible subtask under FWP:
Extraordinary Responsive Magnetic Rare Earth Materials

FWP Number:
AL-90-501-004

Program Scope:
Research is focused on systematic experimental and theoretical studies of the unique magnetic-martensitic phase transformation in $R_5(Si_xGe_{1-x})_4$ materials, where R is Gd and other lanthanides, to achieve an understanding of the underlying electronic structure and the microscopic interactions bringing about extremely strong coupling of the magnetic moments with the lattice. Another goal is to develop and validate models of the magnetic-martensitic transformation, which will allow for the design of novel material systems exhibiting extremely large responses to small changes of magnetic field, temperature, and pressure.

Major Program Achievements (over duration of support):
- In-situ X-ray diffraction of $Gd_5(Si_xGe_{1-x})_4$ for $x \simeq 0.5$ showed that the low temperature martensitic transformation is rapid, complete and fully reversible when it is coupled with the ferromagnetic ordering-disordering process on cooling-heating. A second, high temperature martensitic phase change was discovered between ~500 and 700 K on heating, and it is sluggish, incomplete and irreversible in the paramagnetic state, even though the crystallographic phase change appears to be the same as for the low temperature phase transition.
- Successfully synthesized a number of single-crystal R-Si-Ge (R = lanthanide) compounds.
- Electronic structure calculations for Gd_5Si_4 and Gd_5Ge_4 showed how Si-Si or Ge-Ge bonding is coupled to crystal structure and magnetic structures.
- The electronic properties of ferromagnetic orthorhombic and paramagnetic monoclinic phases of $Gd_5(Si_2Ge_2)$ were calculated using tight-binding linear-muffin-tin-orbital (TB-LMTO) method with combine-correction contribution
- Exchange coupling calculations were used to obtain the effective Heisenberg Model parameters. The free energy as a function of temperature was then calculated in the mean-field approximation and a first order magneto-structural phase transition with a large value of $|\partial M/\partial T|$ was predicted, thus explaining the giant magnetocaloric effect.

Program impact:
This research is being carried out by a multi-disciplinary group of scientists from the Metal and Ceramic Sciences, Condensed Matter Physics and Solid State Chemistry Programs of the Ames Laboratory. With such a group, a number of experimental and theoretical approaches have been brought to bear on these extraordinary $R_5(Si_xGe_{1-x})_4$ materials in order to understand their basic nature.

Interactions:
Efforts on the basic studies of magnetic-martensitic phase transformations are carried out in collaborations with scientists at Moscow State University and the Van der Waals-Zeeman Institute of the University of Amsterdam, the Netherlands.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
K.A. Gschneidner, Jr. – Honorary member of the European rare earth and Actinide Society (1998)
D.C. Jiles – Fellow of the American Physical Society (1997); Magnetics Society Distinguished Lecturer (1997-98)
V.K. Pecharsky – Editor of *Handbook on the Physics and Chemistry of Rare Earths*, 2001-present. Technical Editor of *Advances in Cryogenic Engine*ering, 1999-present.
13 invited talks since 2000

Principal Investigator Commitments for FY2002 to Nearest +/- 10%:
K.A. Gschneidner, Jr. [Co-coordinator] (10%), V.K. Pecharsky [Co-coordinator] (20%), T.A. Lograsso (20%)
J.E. Snyder (20%), D.C. Jiles (10%), L.S. Chumbley (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $100 k **FY01 BA $**859 k **FY02 BA $**842 k

Laboratory Name: Ames
B&R Code: KC-02-01-05

FWP and possible subtask under FWP:
Science of Amorphous and Aperiodic Materials

FWP Number:
AL-90-501-006

Program Scope:
The main scientific goals in this effort are directed toward gaining an increased fundamental understanding of (i) the correlation between short-range atomic order and the devitrification and deformation behavior in amorphous systems and (ii) the role of crystal chemistry (*i.e.*, composition, bonding and coordination) in controlling the structural stability of aperiodic systems. Amorphous and aperiodic structures, while nearly opposite in terms of long-range atomic order, do have significant interrelationships, particularly in regard to short-range atomic order. For instance, meta-stable aperiodic phases (*i.e.*, quasicrystals) have been observed during the devitrification sequence of certain amorphous metallic systems. Non-equilibrium phase formation is often speculated to result from similar atomic structures between the amorphous and devitrified phases.

Major Program Achievements (over duration of support):
- Structural determination of meta-stable crystalline devitrification phase from amorphous $Zr_{70}Pd_{20}Cu_{10.}$
- Discovered the expanded solubility of transition metals in $Zr_{70}Pd_{30}$ at high temperature.
- First to report the synthesis-dependent formation of quasicrystals in amorphous $Zr_{70}Pd_{30}$ and $Zr_{70}Pd_{20}Cu_{10.}$
- Discovered quasicrystalline formation in $Zr_{70}Pd_{20}Cu_{10}$ at 273 K under high strain deformation.
- Synthesized the largest (~0.75 cm^3) $Cd_{84}Yb_{16}$ phase-pure quasicrystalline single grain.
- Determined the basic atomic cluster structure in rare earth-Mg-Zn face-centered icosahedral quasicrystals.

Program impact:
Provided critical insights on the intricate boundaries surrounding glass formation, non-equilibrium phase selection during devitrification and formation of stable aperiodic and related approximant structures. Such insights will enable the development of predictive capabilities using computation, simulation and theoretical approaches.

Interactions:
- Materials Chemistry and Condensed Matter Physics Programs at Ames Laboratory to study surfaces and interfaces of quasicrystals
- Advanced Photon Source (MU-CAT and SRI-CAT) at Argonne National Laboratory to perform dynamic structural investigations with high energy X-ray scattering in real time isothermal modes
- CNRS Laboratoire de Science et Génie des Matériaux et de Métallurgie at the Ecole des Mines de Nancy to analyze the structure of liquid and amorphous metallic alloys using neutron scattering techniques
- Yonsei University, Center for Non-Crystalline Materials to understand interfacial influence on shear band behavior
- Institut Fur Metallische Werkstoffe (IFW), Dresden to examine solid state synthesis and related devitrification behavior of amorphous metallic alloys
- Brookhaven National Laboratory to perform high resolution transmission electron microscopy on R-Mg-Zn and Yb-Cd quasicrystals
- Swiss Federal Institute of Technology Zurich (ETH Zurich) to study phase stability of quasicrystals at high temperatures

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
M.J. Kramer – Member of Spallation Neutron Source POW-GEN3 Instrument Advisory Team,
D.J. Sordelet – Chair, 9th International Conference on Quasicrystal (2004),
15 invited talks since 2000

Principal Investigator Commitments for FY2002 to Nearest +/- 10%:
D.J. Sordelet [Coordinator] (20%), J.C. Foley (80%), S.B. Biner (20%), M.J. Kramer (40%), J.R. Morris (20%), L.S. Chumbley (30%), T.A. Lograsso (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA ~$134 k **FY01 BA** ~$186 k **FY02 BA $**725 k*

* The significant increase in funding was a result of an FY02 restructuring of the research efforts within the Program and the formation of an *Amorphous and Aperiodic Materials* focus area..

Laboratory Name: Ames Laboratory
B&R Code: KC020301

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP:
Neutron Scattering

FWP Number: AL-90-540-001

Program Scope: A variety of neutron scattering techniques are used to study structure, dynamics, and magnetism in hard and soft condensed matter. We explore structural phase transitions, lattice dynamics, magnetic structures, and magnetic excitations in exotic materials – such as superconductors, low dimensional magnetic systems, ionic conductors and complex magnetic materials. We also apply reflectivity, inelastic scattering techniques to investigate molecular magnets, and thin organic films.

Major Program Achievements (over duration of support):
Determined magnetic critical behavior Li-Orthophosphates – and ionic conductor Li-phosphate. An incommensurate-commensurate phase transition in $LiNiPO_4$ was discovered and correlated with anomalies in the measured magneto-electric effect. Small modifications to the magnetic structure of $LiCoPO_4$ were found and the critical behavior of this system was compared to theories of low dimensional systems. Neutron scattering studies of superconducting $YBa_2Cu_3O_7$ under external magnetic field reveal possible short range antiferromagnetic order, which we hypothesized is due to AF correlations in vortex cores. A newly commissioned liquid surface diffractometer at the Advanced Photon Source synchrotron has been exploited to the study of biomimetic membranes. Structures of dendritic polymers at gas/water interface were determined as the polymers increase in length. Sphingolipids were studied in relation to their cellular function. A major component of our effort in the last couple of years was the upgrading of the HB1-A Ames Laboratory triple-axis spectrometer presently being installed at the HFIR and our active participation in the IDT's for the HYSPEC and SEQUOIA spectrometers for SNS.

Program Impact:
Our neutron scattering findings in cuprates and related oxides shed light on the interplay between magnetism and superconductivity of the High Tc superconductors. As some of these oxides exhibit properties characteristic of two-dimensional spin S=1/2 models, they are important validity checks for several many-body theories. Our neutron scattering studies on Li-orthophosphates can explain long-standing questions regarding the magneto-electric effect in these systems. Neutron structural and magnetic studies of a of Li-phosphates ionic conductors help understand the effects of substitutions/vacancies on the ionic conductivity. X-ray and neutron scattering from bio-organic films are crucial for establishing the relationship between structure and function in a variety of lipids and proteins. These studies are relevant for understanding biological processes on the molecular level in environments that very close to those of living cells. The liquid surfaces diffractometer is in demand for beamtime by biophysicists, chemical engineers, and others for studies of biological systems and for nano-science.

Interactions:
Internal— Materials Preparation Center, numerous Ames Lab groups dealing with magnetic materials (Johnston, Canfield, Koegerler, Gschneidner, Goldman, etc.)
External—Oak Ridge National Laboratory (including neutron scattering); Chemistry Department, University of Geneva, Switzerland, Physical Chemistry, University of Bilboa, Spain, Physics Department, Campinas Brazil, Physics Department, Leiptzig University, Germany.

Recognitions, Honors and Awards (at least in some part attributable to support under this program
C. Stassis – Executive committee and membership secretary, NSSA; Executive Committee SNS and HFIR users group; Fellow of the APS.
D. Vaknin – Executive Committee, SNS and HFIR users' group. Neutron Biology Task Force (advising the SNS on structural biology issues).

Personnel Commitments for FY2002 to Nearest +/- 10%:
C. Stassis (50%), D. Vaknin (100%), J. Zarestky (100%)

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA \$443k **FY01BA** \$440k **FY02 BA** \$460k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP:
X-ray Physics

FWP Number: AL-90-540-001

Program Scope:
The structural characterization of materials and the investigation of structural changes associated with, or leading to, novel behavior of materials. The emphasis has been on elucidating the properties of quasicrystalline materials, and in the determination of magnetic structure.

Major Program Achievements (over duration of support):
We have recently concentrated on developing the techniques to make x-ray scattering determinations of magnetic structure a practical alternative to neutron scattering measurements. This is particularly important for those samples and conditions that are not well suited to neutron measurements such as compounds with neutron-opaque elements, single crystal measurements of small samples, and investigations of surface magnetism. The work of our group over the past few years in exploiting resonant and non-resonant magnetic x-ray scattering for ab-initio magnetic structure determination has contributed very significantly to this goal. Since resonant scattering occurs at well-defined energies (absorption edges) for different elements, the local magnetism associated with particular magnetic species in a mixed system can be investigated separately. Finally, our group has shown that by exploiting the angular dependence of the cross- sections for resonant and non-resonant scattering, a complete determination of the spatial components of the ordered moment can be accomplished. We have demonstrated this in a series of systems including RNi_2B_2C, RNi_2Ge_2, RCu_2Ge_2 (R=Ho, Gd, Nd, Sm, Tb). We have also exploited the fact that the quadrupole (4f to 5d) transitions are present in magnetic circular dichroic spectra and can yield information about the temperature dependence of the 4f moment separate from that of the 5d conduction electron magnetic moments.

Program Impact: Graduate on average one student per year, trained in x-ray scattering techniques. Many of our ideas and experience for magnetic scattering have been used to design, construct, and commission the facilities at the MUCAT undulator beamline at the Adanced Photon Source. Similarly, our experience was instrumental in the development of a state-of-the-art high temperature powder diffractometer for investigations of thermal expansion, phase transitions, and growth kinetics of high temperature (>1500C) alloys. An advanced version of this instrument was recently commissioned at the MUCAT beamline.

Interactions:
Internal – Strong interactions with groups in Materials Chemistry and Metallurgy and Ceramics, (e.g. the high temperature diffractometer was built in collaboration with Matthew Kramer and R. W. McCallum (Met. and Cer). Recent strong collaborations with P. A. Thiel's group in Materials Chemistry on Quasicrystal Surfaces have been particularly fruitful.
External – SRI CAT (Argonne), KFA (Juelich, Germany), ESRF (France)

Recognitions, Honors and Awards (in some part attributable to support under this program):
Goldman is a Fellow of the American Physical Society and gave five invited talks last year; two at international workshops. He is Director of the MUCAT (Midwest Universities Collaborative Access Team) beamline at the Advance Photon Souce.

Personnel Commitments for FY2002 to Nearest +/- 10%:
A. I. Goldman (PI-20%), Antoine Letoublon (PD-100%), Students: William Good (100%), Jong-Woo Kim (100%), Lizhi Tan (50%), technician: Marc McGinn (25%).

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $170k **FY01 BA $**125k **FY02 BA $**125k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-01

FWP and possible subtask under FWP: MUCAT

FWP Number: AL-00-540-019

Program Scope: The Midwest Universities Collaborative Access Team (MUCAT) was organized for the purpose of developing and operating a sector (insertion device and bending magnet lines) at the Advanced Photon Source. MUCAT secured funding for the construction of the undulator line in FY96 and saw first light in the First Optics Enclosure in February 1998. Commissioning experiments on the main undulator line began late in FY99. The undulator line presently consists of two experimental stations in tandem for x-ray studies in the 3-40 keV energy range. A high-energy side station (30- 130keV), funded by FZ Juelich, is in the latter stages of commissioning, allowing simultaneous operations of the main line and side station. In FY2000, the Department of Energy accepted our proposal to construct a bending magnet beam line in Sector Six. The construction of this facility is in progress.

This consortium brings together scientists from several universities, national and international laboratories with common interests in the use of synchrotron radiation for materials science research. The magnetic scattering and spectroscopy portion of the scientific program concentrates on resonant and nonresonant scattering studies of magnetic materials. Resonant and nonresonant magnetic x-ray scattering measurements offer important and complementary means of determining magnetic structures in materials which are ill-suited, by reasons of size or chemical composition, to traditional neutron measurements. Research efforts in the surface scattering program are centered on the study of the kinetics and growth of 2-dimensional systems, the role of defects in epitaxy, ordered non-epitaxial overlayers, phase transitions and investigations of liquid surfaces. The brilliance of undulator radiation obviates the need for strong focusing of the beam, resulting in a small footprint on the sample with low divergence. A liquid surface diffractometer is used to probe the chemistry and physics of monolayer films at liquid surfaces as well as realistic models of biological membranes and their reaction to various stimuli and environments. High energy x-rays are used for in-situ studies of materials processing using a new high temperature furnace constructed at the Ames Laboratory and studies of pair distribution functions of poorly or partially ordered structures.

Current Capabilities
There are currently three experimental stations in the sector. The four-circle diffractometer and liquid surface diffractometer in 6-ID-B have been declared operational (November 2000 and November 2001 respectively) while the commissioning phases for the high-energy side station (6-ID-D) and surface science station (6-ID-C) are nearly complete. At the same time, we are developing the bending magnet beam line (6-BM-A,B) in the sector. Further details of the status of each section are given below:

Program Impact: Has enabled high quality x-ray measurements of static structure magnetic structure and structural transformations. A DOE review of the initial progress takes place November 21, 2002.

Interactions:
Internal—Solid State Division, Alloy Behavior and Design Group, X-ray Research and Applications Group, Structural Ceramics Group, … .
External— Member institutions: Ames Laboratory/Iowa State, U. of Missouri, Georgia Tech, Washington U., U. of Wisconsin, Kent State, SUNY Stony Brook, Michigan State, and FZ Juelich in Germany.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
This is a new program, with experiments just beginning in the last year.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Douglas Robinson (100%), Didier Wermeille (100%), Eric Zoellner (100%)

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $377k **FY01 BA $**450k **FY02 BA** $450k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP:
NMR-NQR investigation of new materials and phases

FWP Number AL-90-540-002

Program Scope:
Measurements of NMR-NQR spectra and relaxation aimed at investigating the magnetic, electronic and structural microscopic properties on new materials and phases, including: the electronic structure of the normal phase in new superconductors and strongly correlated metals and alloys. the flux line dynamics in the superconducting phase, the hopping dynamics of light ions in fast ionic conductors and of hydrogen in metal hydrides, and the classical and quantum spin dynamics in single molecule nanomagnets.

Major Program Achievements (over duration of support):
1) Elucidation of the phase diagram and of the magnetic properties of $La_{2-x}Sr_xCuO_4$ at low concentrations of Sr impurities including the evidence for the microsegregation of the doped holes and the cluster spin glass phase. 2) Obtained information about the density of states and the symmetry of the conduction electron wave function at the Fermi level in MgB_2 and AlB_2. 3) Clarified some aspects of the hopping dynamics in new glassy fast ion conductors based on lithium, silver and boron oxides and sufides in the temperature and composition range in which deviations of the conductivity for Arrhenius behavior are observed. 4) Determination of the systematics of hydrogen diffusivity by the first model-independent pulsed- field- gradient (PFG) measurements on the hydrides and deuterides of Y,La,Ti,Zr.Hf, and on Laves phase hydrides, e.g. ZrV_2H_x . 5) Confirmation of the orientation of the local spins in the high total spin ground state of the molecular magnets Mn_{12} and Fe_8. Evidence for the rigidity of the spin configuration in presence of canting of the total magnetization of the molecule in high external magnetic fields. 6) Novel method which utilizes the NMR signal to monitor the slow relaxation of the magnetization of molecular magnets in the superparamagnetic state at low temperature. Evidence for quantum tunneling dynamics. 7) Cross relaxation between the nuclear Zeeman reservoir and the magnetic levels of the magnetic molecule: a valuable method to investigate the fluctuations of the magnetization at level crossings, including quantum dynamical effects.

Program impact:
Provided valuable information about magnetic and electronic properties of the systems investigated and about the ion dynamics in fast ion conductors and the proton dynamics in metal-hydrogen systems.
The NMR methods and the interpretation paradigms developed in the study of magnetic molecules have been adopted by other research laboratories around the world .

Interactions:
Internal – Other CMP groups within Ames Laboratory: Johnston, Canfield, Luban, Tringides. Department of Material Science and Engineering
External – University of Pavia, Italy; University of Hokkaido, Japan; High Magnetic Field Center in Grenoble, France; University of Trondheim, Norway; University of Florence and Modena , Italy; Max-Planck-Institute for Metals Research, Stuttgart, Germany

Recognitions, Honors and Awards (at least partly attributable to support under this program):
F.Borsa – Fellow of the American Physical Society (2001). Fellowship of the Japan Society for the Promotion of Science (1998) Member of the Program Committee of the International Conference on Magnetism , Rome 2003.

Personnel Commitments for FY2002 to Nearest +/- 10%:
F.Borsa (group leader) 50%, B. Suh (16%), R.Vincent (visiting scientist) 50%, D.Procissi, S.H.Baek, H.Tanaka (students) 50%, R.G.Barnes (Emeritus Professor) 20%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $198k **FY01 BA** $236k **FY02 BA** $211k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experimental
Correlated states in magnetic materials

FWP Number: AL-90-540-002

Program Scope:
Design, discover, grow and characterize novel materials with exotic / interesting physical properties (generally electronic / magnetic).

Major Program Achievements (over duration of support):
Over the past three fiscal years this program has been studying a wide range of intermetallic systems which manifested magnetic and / or superconducting ground states. This program continues to be a world leader in the study of the RNi2B2C family of magnetic superconductors. In addition, this program's work on the growth and properties of single grain quasicrystals (including the magnetic RMgZn family) has revolutionized research into stable quasicrystalline materials. Over this three year period this group has continued to design and study the magnetic properties of materials with highly anisotropic local moments and used these systems to address question in the fields of metamagnetism as well as spin-glass physics. Most recently, since January 2001, this program has been a world leader in the synthesis and characterization of MgB2, the binary intermetallic superconductor with Tc~40 K. Our first three Physical Review Letters (published in Feb. and Mar. of 2001) delineated the mechanism of the superconductivity, range of the superconducting state and salient physical length scales, and demonstrated a simply synthetic route to making powders, wires and films.

Program impact:
126 publications between Jan. 2000 and Oct. 2002 (as well as one patent filed on processing of MgB2)
43 *Physical Review B*, 11 *Physical Review Letters*, as well as smaller numbers of papers in journals such as *Physica C, Physica B, Nature, J. Alloys and Comp., and Physics World*. These papers have been cited (in published articles) over 600 times since their writing. (~ 400 of these citations are to the first three PRLs published by our group on MgB_2.) Given that these are all very recent papers such a high citation rate is a strong indication of a large impact.

Interactions:
Internal: Ames Laboratory groups in CMP, Materials Chemistry, and Metallurgy and Ceramics
External: Lucent / Bell Labs, Riso, Stanford, National High Magnetic Field Lab, U. C. Riverside, ESRF (Grenoble), ILL (Grenoble), CEA (Grenoble), CNRS (Grenoble), Brookhaven National Laboratory, ETH (Zurich), as well as dozens of other labs and universities through out the world.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Physical Society (PCC)
Divisional Associate Editor for *Phys. Rev. Lett*. (PCC)
Over 30 invited talks / colloquium
Invitations to write articles for *Physics World, Physics Today*, and encyclopedia entries on MgB_2

Personnel Commitments for FY2002 to Nearest +/- 10%:
Paul Canfield (8%), Staff: Sergey L. Bud'ko (65%); Post Docs: Cedomir Petrovic(100%), Raquel Ribeiro (100%); Students: Emilia Morosan (28%), Derek Wilke (28%), Chung-Wang Gao (27%). Lizhi Tan (3%), Norman Anderson Jr. (12%), Nate Kelso (3%), Joel Strand (21%), Hahnbit Rhee (14%); Technician: Marc McGinn (40%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$383k **FY01 BA** \$509k **FY02 BA** \$478k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics; New Materials

FWP Number: AL-90-540-002

Program Scope: Synthesis and study of new oxide and other materials with potentially novel electronic and/or magnetic properties. Characterization of the materials using x-ray diffraction, magnetization, magnetic susceptibility, specific heat, thermal expansion, electronic transport, thermogravimetric analysis, and differential thermal analysis measurements. Theoretical modeling of the properties. Provision of high-quality single crystal and polycrystalline samples to other groups for measurements of additional properties.

Major Program Achievements (over duration of support): Provided high-quality single crystals of $(Ca,Sr)_2CuO_2Cl_2$ for measurements by various other groups. Continued the search for *d*-electron metallic oxides to expand the new class of *d*-electron heavy fermion materials that we created in 1997 by the discovery of heavy fermion behavior in the spinel-structure compound LiV_2O_4. Discovered a new series of compounds $Lu_2V_2O_{7-x}$ ($0 < x < 1$) derived from the known spin-1/2 insulating ferromagnetic pyrochlore-structure compound $Lu_2V_2O_7$. Completed experimental and theoretical magnetic susceptibility studies of the exchange interactions in the insulating quasi-one-dimensional (1D) spin-1/2 oxide spin ladder compounds $SrCu_2O_3$, $Sr_2Cu_3O_5$, $LaCuO_{2.5}$, and $(Ca,Mg)V_2O_5$ and the quasi-1D chain compound NaV_2O_5. Grew large single crystals of the spin-1/2 vanadium zig-zag chain compound LiV_2O_5 using fused-salt electrolysis. Carried out magnetization and modeling studies of the spin-1/2 alternating-exchange chain compound $(VO)_2P_2O_7$. Searched for new superconducting and/or metallic doped oxides synthesized by room-temperature chemical and electrochemical aqueous and nonaqueous redox reactions with 1D or 2D undoped insulating spin-1/2 oxide parent compounds. Performed magnetization and EPR measurements and modeling of the spin-1/2 compound $Sr_2Cu(OH)_6$, which is the decomposition product of the reaction of the 1D spin-1/2 chain compound Sr_2CuO_3 with water. Completed thermodynamic and transport measurements and modeling on a large single-grain $Al_{71}Pd_{21}Mn_{08}$ quasicrystal and its crystalline $Al_{72}Pd_{25}Mn_{03}$ approximant.

Program impact: Our discovery of *d*-electron heavy fermion behavior in LiV_2O_4 continues to attract considerable experimental and theoretical attention. The second member of this class of *d*-electron heavy fermion compounds, $(Ca_{0.7}Sr_{0.3})_2RuO_4$, was reported this year by a group at ORNL. We are confident that our ongoing search for new and/or improved interesting materials will continue to yield results with potentially significant impacts. Our magnetic susceptibility studies of the cuprate spin ladder compounds led to identification of the four-spin ring-exchange interaction as important to the magnetic properties, and by extrapolation, to those of the layered cuprate high temperature superconductor family of compounds. This interaction is increasingly recognized as important to interpreting the results of various measurements on cuprate materials. The above quasicrystal measurements demonstrated the occurrence of very soft phonons that are not detected by current neutron scattering techniques.

Interactions:
Internal - Ames Lab (N. Anderson, Jr., F. Borsa, P. Canfield, B. Cook, B. Harmon, R. Jacobson, T. Lograsso, D. Lynch, C. Olson, K. Ruedenberg, A. Russell, D. Vaknin, J. Zarestky);
External - LANL (A. Migliori); U. Tokyo, Kyoto U., ETH Zürich, Dortmund U. Crystals sent to various groups, e.g. Z.-X. Shen (Stanford) and J. Fink (Dresden).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Distinguished Professor of Liberal Arts and Sciences, ISU, 2000, to D. C. Johnston
1 invited talk during FY2002, Fellow of the American Physical Society

Personnel Commitments for FY2002 to Nearest +/- 10%:
D. C. Johnston (group leader-20%), L. L. Miller (Assoc. Scientist-90%); C. A. Swenson (Associate, 20%); J. M. Hill (PhD student, 100%); M. Fitzpatrick (student-40%); G. Knoke (undergraduate 10%); M. Todd (undergraduate-10%); S. Madison (undergraduate, NSF REU program, 10 weeks, summer 2002) 20%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$239k **FY01 BA** \$276k **FY02 BA \$**252k

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Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics, Experiment.
Optical and Spectroscopic Properties of Solids and Surfaces

FWP Number: AL-90-540-002

Program Scope:
Angle-resolved photoelectron spectroscopy at the Synchrotron Radiation Center is used to elucidate the electronic structure of solids. Materials studied are generally metallic, and often are systems in which electron correlation is important. Examples include cuprate superconductors, Ce and Ce-based intermetallic compounds, Heusler alloys, low-dimensional crystals.

Major Program Achievements (over duration of support):
First recognition (simultaneously with IBM group) that both peaks in Ce and Ce compounds arise from the 4f electron. First observation of the superconducting gap in any cuprate by photoelectron spectroscopy (or any technique). Early band mapping of two cuprates. Emphasis of the importance of dipole matrix elements in photoelectron spectroscopy. Demonstration of weak dispersion in 4f bands CeSb, LaSb (via hybridization). First demonstration of dispersion, hence band-like states, in a quasicrystal.

Program impact:
Characterization of electronic states, often including band mapping, led to better understanding of correlation in Ce-based systems. Convinced others of importance of dipole matrix elements. Early band mapping of cuprates and observation of superconducting gap attracted wide interest.

Interactions:
Internal: P. C. Canfield, T. Lograsso, V. Atropov, B. N. Harmon
External: A. J. Arko, J. J. Joyce, J. Sarrao (Los Alamos National Lab), J. W. Allen (Univ. of Michigan), R. Liu (Michigan State Univ.), D.McIlroy (Univ. of Idaho), D.M. Wieliczka (Univ. of Missouri – Kansas City), M. B. Maple (Univ. of California – San Diego), Z. Fisk (Florida State Univ.), J. C. Campuzano (Argonne Nat. Lab), J. Tobin (Lawrence Livermore Nat. Lab), J.-S. Kang (Catholic University of Korea), R. Manzke (Freie Univ.- Berlin), M. Piacentini, (Univ.of Rome I)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
66 invited talks since the inception of the photoelectron spectroscopy program.
Olson and Lynch are both Fellows of the American Physical Society

Personnel Commitments for FY2002 to Nearest +/- 10%:

D. W. Lynch (40%), C. G. Olson (100%), Joong-Mok (student-50%), Jongik Park (student-50%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $430k **FY01 BA** $351 **FY02 BA** $345k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP:
Correlated states in magnetic materials – magneto-optics

FWP Number: AL-90-540-002

Program Scope:
Magneto-optic Kerr (MOKE) spectra are measured over an energy range of 0.5 – 5 eV on samples in fields up to 7T at temperatures between 2.5 and 300 K. In order to extract the off-diagonal component of the conductivity, the dielectric functions are measured at 300 K by spectroscopic ellipsometry. Materials studied are obviously ferro- or ferrimagnets. Most contain a rare earth, or a transition metal, or both. First principles electronic structure calculations are performed to understand the often subtle MO spectra, and the magnetic x-ray dichroism and resonant scattering spectra.

Major Program Achievements (over duration of support):
Measurement of Kerr spectra for over a dozen intermetallic compounds, successful calculation of such spectra. Observation of a metamagnetic (ferro- to antiferromagnetic) transition in $Ce(Fe_{0.9}Co_{0.1})_2$ by magneto-optic spectroscopy and MOKE spectrum in AF phase. We made the first calculations of MO spectra employing the LDA+U technique to allow treatment of correlated electron states. The calculations were very successful for magnetite (Fe3O4), and for a series of mixed valent materials (Tm monochalcogenides, SmS, ThB6, etc.). Spectra were also calculated for planned magnetic x-ray circular dichroism experiments for Gd5Si2Ge2, the complex magnetic refrigeration material being investigated by Karl Gschneidner's group. Likewise, regular MO spectra were calculated in anticipation of good single crystals for temperature dependent MO experiments.

Program impact:
Systematic study of several series of compounds shows rare earth states rarely participate directly in MOKE spectra, but their moments polarize other electrons. The off-diagonal component of the dielectric function, proportional to the magnetization, can be calculated rather accurately as long as 4f states do not lie within a few eV of the Fermi level, or if the LDA+U technique is used to account for the strong correlations of the 4f electrons. Actually the LDA+U approach is simply a technique for positioning the 4f states which allows them to interact appropriately with the conduction band states. The agreement with experiment is impressive and lends strong support for the LDA+U approach for optical spectral analysis. The success of theory in experiment in this area is excellent and we signed a contract to write a book reviewing the field in light of several recent advances.

Interactions:
Internal: T. Lograsso, P. C. Canfield, J. Anderegg, A. Goldman
External: J.-Y Rhee (Hoseo University, S. Korea), A. Sievers (Cornell), M. Dovobrotvorska (Kharkov)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
5 invited talks, and a book contract for a review of magneto-optics (11/21/02). Lynch and Harmon are Fellows of the APS.

Personnel Commitments for FY2002 to Nearest +/- 10%:
D. W. Lynch (10%), B. Harmon (5%), V. Antropov (30%), V. Antonov (visiting scientist, 30%), J.Y. Rhee (visiting professor, 10%).

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $125k **FY01 BA** $105k **FY02 BA** $95k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP:
Photonic Band Gap Materials

FWP Number: AL-90-540-002

Program Scope:
To design, model, fabricate periodic structures resulting in photonic band gap crystals.

Major Program Achievements (over duration of support):
Design and development of directional antennas fabricated from cavities in PBG crystals at microwave frequencies in collaboration with Ekmel Ozbay's group at Bilkent University. Collaboration with Shawn Lin and Jim Fleming at Sandia National Laboratory: Three dimensional waveguide networks in layer-by-layer silicon photonic crystals. Tungsten metallic photonic crystals fabricated at Sandia and designed at Ames may lead the way to very energy efficient lighting system. Development of economic microtransfer molding method for fabrication of 3d layer-by-layer photonic crystals: 4 layer titania crystal achieved, however, problems in accurate alignment of layers need to be addressed in further work. Measurement of propagation loss in straight 3d PBG waveguide and perpendicular waveguide bends at microwave X-band frequencies. Development of efficient infrared emitter for efficient sensor device in collaboration with scientists at Ion Optics. Finite difference time domain calculations of finite 2d photonic crystal for design of waveguides and a resonant cavities. Fabrication of far infrared metallic periodic and disordered PBGs by the LIGA technique: collaboration with research center at Crete

Program impact:
Our group was one of the pioneers in the field of photonic crystals and continues to play a major role in leading the development in this field.

Interactions:
Hong Kong University of Science and Technology, Sandia National Laboratory, Agilent Laboratory (Palo Alto), DOE nanoscience network (participants from 7 national laboratories), Bilkent Univeristy, Turkey, Ion Optics, Research Center of Crete, Ecole Polytechnique, and other members of the PCIC European collaboration, Univ. of Twente, Netherlands, and Universitat Karlsruhe, Germany

Recognitions, Honors and Awards (attributable to support under this FWP or subtask):
Energy 100 Award and Science 100 Award, U. S. Dept. of Energy, 34 papers (1 in Nature), 27 invited talks, organized three international conferences, 2 U.S. Patents issued, one in process
Costas Soukoulis :Fellow of **AAAS**, 2002,Senior Alexander von Humboldt Award, Iowa State University. Outstanding Achievement in Research, 2001, editor of the new journal *Photonics and Nanostructures: Fundamentals and Applications* 2002. Both Ho and Soukoulis are fellows of the APS.
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Personnel Commitments for FY2002 to nearest +/- 10%:
Theory: K. M. Ho (5%), C. M. Soukoulis (6%), R. Biswas (50%), Z. Y. Li (60%), I. El-Kady (20%), S.Foteinopoulou (38%), M. Agio (8%), M. Kafesaki (unpaid),
Experiment: G. Tuttle (unpaid), K. Constant (10%), D. Cann(10%), W. Leung (100%), H. Kang (50%), C. H. Kim (25%), C. Sell (50%), Y.S. Kim (30%), M. al-Shorman (40%), T. Lloyd (10%), S. Dudley (10%), M. Dau (10%), E. Jackson (10%), J. Penley (10%), M. Su (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $460k **FY01 BA** $404k **FY02 BA** $453k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Experimental Solid State Physics
Photophysics of luminescent organic semiconductors and organic light-emitting devices (OLEDs)

FWP Number: AL-90-540-002

Program Scope:
Fabrication of π-conjugated thin films and OLEDs, and optoelectronic studies thereof. The films are studied by photoluminescence (PL)- and PL- and photoinduced absorption (PA)-detected magnetic resonance (PLDMR and PADMR, respectively). The OLEDs are studied by current- and electroluminescence (EL)-voltage measurements, and by EL- and electrically (i.e., current)-detected magnetic resonance (ELDMR and EDMR, respectively).

Major Program Achievements (over duration of support):
- The PLDMR and PADMR studies identified the nonradiative quenching of the singlet excitons by polarons and triplet excitons as the major mechanism responsible for the decrease in the PL and EL efficiency at high excitation density or high injection currents.
- The ELDMR and EDMR studies showed that a charged layer at the organic-cathode interface may be responsible for the major role of that interface in determining the performance of the OLED.
- Other efforts on OLEDs resulted in the development of combinatorial methods for optimizing the fabrication parameters of various OLEDs.
- We developed the shortest wavelength UV-violet OLEDs reported to date, and optimized their fabrication using a combinatorial approach.
- We succeeded in developing the most intense white OLEDs reported to date, with a brightness that exceeded 54,000 Cd/m^2, a factor of 25 more than conventional light sources.
- We discovered and studied strong positive spikes at the turn-off of the transient blue EL induced by short voltage pulses.
- We invented a new platform for fluorescent chemical sensors and sensor arrays, by structural integration of the sensor film with an OLED light-source.

Program impact:
Our various optically detected magnetic resonance studies identified two PL and EL quenching mechanisms which strongly impact the performance of PL for films and of EL for OLEDs. Our other studies on OLEDs underpin the science for the development of OLEDs for solid-state lighting, development of low-cost ultrafast pulsed light-sources, and a offer a new platform for chemical sensors and microsensor arrays.

Interactions:
External - Institut für Festkörperphysik, Technische Universität, Graz, Austria; Chemistry Department, University of Michigan; Department of Electical Engineering, MIT; Department of Chemistry, MIT; Department of Physics, University of Utah; The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel; and the Department of Applied Physics and Materials Science, City University of Hong Kong.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
33 Invited talks at various national and international conferences, and at academic institutions and industrial labs in the US and abroad.

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. Shinar, PI, 25%; Graduate students, 4.5 FTE

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $175k **FY01 BA** $150k **FY02 BA** $192k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics
Synthesis, Experiment, and Theory of Magnetic Molecules

FWP Number: AL-90-540-002

Program Scope: Complementary experimental and theoretical methods are used to understand both static and dynamical properties of magnetic molecules, especially polyoxometalate clusters, isolated as pure crystalline materials. These inorganic materials allow for research on magnetism at the nanoscale level. Modifications of the synthesis process yield a wide range of distinct, controlled spin designs. Experimental studies utilize thermodynamic, magnetic resonance (NMR, EPR, muSR), optical, and neutron methods. Theoretical studies develop and utilize analytical and simulational methods applied to classical and quantum models.

Major Program Achievements (over duration of support):
Synthesis of over 20 novel compounds of magnetic molecules and their full chemical characterization, including highly symmetric frustrated spin systems and the first polyoxomolybdate-based single molecular magnets. Comprehensive characterization and detailed microscopic theory of mesoscopic paramagnetism in $\{Mo_{72}Fe_{30}\}$ Keplerate compound and its derivatives. Experimental and theoretical evidence for long-range magnetic order in strongly coupled layer magnetic molecule systems. Utilization of NMR methods for exploration of spin-level crossings and quantum tunneling in magnetic molecules. Comprehensive theoretical explanation of quantum decoherence and tunneling phenomena in $\{V_{15}\}$ system. NMR and theoretical evidence for critical slowing-down in antiferromagnetic magnetic molecules. Development of high-temperature susceptibility expansion methods for the determination of exchange parameters in complex magnetic molecules. Development of computational code for static and dynamical properties of large classical Heisenberg spin systems.

Program Impact:
Over 70 scientific articles on magnetic molecules between 1998-2002. The Ames Lab group and their collaborators is one of the broadest and most active research groups in the U.S. on magnetic molecules.

Interactions:
Internal - S. Bud'ko, P.C. Canfield, D.C. Johnston, W. McCallum, R. Modler,
External - LANL, National High Field Laboratory (Tallahassee), ORNL, U. of Missouri, U. of Bielefeld (Germany), U. of Osnabrück (Germany), U. of Pavia (Italy), U. of Glasgow (UK), U. of Manchester (UK), U. of Hokkaido (Japan), U. of Nijmegen (Netherlands), U. of Gronigen (Netherlands), ILL (Grenoble), U. of Bern (Switzerland).

Recognitions, Honors and Awards (at least partly attributable to support under this program):
12 invited talks in 2002 at universities, workshops, and conferences world-wide; organization of focused sessions at MMM conference and March meeting; DOE nano-science proposal funded (increased effort started end of FY02).

Personnel Commitments for FY2002 to Nearest +/- 10%
F. Borsa (PI-10%), V. Dobrovitski (staff scientist-20%), V. Garlea (post-doc), B. Harmon (PI-5%), P. Kögerler (PI-100%), M. Luban (PI-20%), D. Procissi (grad student), C. Stassis (PI-5%), C. Schröder (post-doc), J. Zarestky (staff scientist-10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $140k **FY01 BA** $140k **FY02BA**$190k

Laboratory name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics, Experiment.
Surface Physics

FWP Number: AL-90-540-002

Program scope:
Characterization and control of atomic scale structures grown on clean surfaces with two complementary techniques, Scanning Tunneling Microscopy (STM) and High Resolution LEED. The control of the geometry and size of such structures requires an understanding of the key microscopic processes operating, such as surface diffusion, nucleation, island formation, etc. The goal of our experiments is to attain such understanding and to use it to facilitate growth of custom-made materials of reduced dimensions which are relevant to nanotechnology applications.

Major Program Achievements (over duration of support):
Discovery of self-organized, uniform height flat-top Pb islands on Si(111) during low temperatures growth as a result of Quantum Size Effects (QSE). Identification of the factors which determine the selected height, so the island height can be easily controlled. The factors are: the substrate interface (i.e. Si(7x7) vs Si(111)-Pb√3x√3), the substrate temperature and the deposited Pb coverage. Correlation between real space and electronic structure of clean stepped Si(111)-(7x7), measured with STM spectroscopy and verified with tight binding calculations. Development of High Resolution LEED as a real time, ultrafast acquisition method to study equilibrium dynamics on surfaces. Determination of interlayer parameters for Ag/Ag(111) which control the 3-d growth mode during epitaxial growth.

Program Impact:
Our work on growth and surface diffusion is well recognized internationally, as evidenced by the number of invited talks and the organization of two major international conferences (Rhodes(Greece) in 1996 and Prague in 2000). The discovery of the uniform height island growth on Pb/Si(111) two years ago has generated worldwide interest with five other groups currently working on this system: Tsong (Taiwan), Chiang (Illinois), Weitering (Oak Ridge), Chou(Georgia Tech), Jalochowski (Poland).

Interactions:
Locally: C. Z.Wang , K.-M. Ho, J.Schmalian, C. Olson, D. W. Lynch
Outside: Ed Conrad (Georgia Tech), T.Rahman (Kansas State), Z. Chvoj (Academy of Sciences, Czech Republic), Z.Zhang(Oak Ridge), J. Wendelken(Oak Ridge) M. Henzler (Hannover, Germany), M. Hon-von-Hogen (Essen Germany), M. Jalochowski (Lublin, Poland), K. Roos (Bradley).

Recognition:
- 3 *Physical Review Letters* and 2 *Rapid Communications* in the last 3 years
- 10 invited talks at international meetings and institutions
- co-edited two conference books.

Personnel Commintements for FY2002 to Nearest +/-10%:
M. C. Tringides(25%) group leader, M. Hupalo(100%) staff scientist, V. Yeh (50%) PhD student.

Authorized Budget (BA) for FY00,FY01,FY02:
FY00 BA $199k **FY01 BA** $178k **FY02BA**$194k

Laboratory Name:Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Theory
Optical and Surface Physics

FWP Number: AL-90-540-003

Program Scope: To study the structure, dynamics, and electronic properties of solid surfaces using a combination of first-principles density functional calculations and atomistic modeling with tight-binding molecular dynamics simulations. Accurate and transferable environment-dependent tight-binding potentials are developed for accurate descriptions of surface properties. A novel tight-binding/genetic-algorithm scheme is used for efficient atomistic structure optimization on surfaces..

Major Program Achievements (over duration of support):
<u>Rocking, diffusion, and intermixing of addimer on Si(001) surface</u>: We proposed a mixed SiGe addimer model for the initial growth of Ge deposition on Si(001) surface based on first-principles calculations. We also discovered several low-energy diffusion pathways for Si addimer and Ge addimer diffusion on Si(001) surface that were overlooked in previous studies. We have also obtained detailed results on the atomic processes involved in the diffusion and intermixing of SiGe addimers on the Si(001) surface.
<u>Atomistic Simulations of Laser Ablation of Diamond Surfaces:</u> We have performed tight-binding molecular dynamics simulations to study the atomic dynamics of diamond surfaces under laser irradiation. Our simulation results show that under nanosecond or longer laser pulses, the diamond (111) surface graphitizes via formation of graphite-diamond interfaces, leading to a dirty surface after the laser treatment. By contrast, with femtosecond laser pulses, graphitization of the surface is found to occur in a layer-by-layer fashion, resulting in a clean surface after the process. This atomistic picture provides an explanation of recent laser ablation experiments which revealed that femtoscond pulses “cleaned” the surface.
<u>Formation and stability of Pb nanostructures on Si(111) surface:</u> In collaboration with Tringides' (Ames Laboratory), we have investigated the effects of subtrate structure on the formation and stability of Pb nanostructures on Si(111). Our study shows that Pb islands on Si(111) surface exhibit certain specially stable "magic" thicknesses due to the quantum confinement of electrons in the island film. The thicknesses of these magic layers depend on the structure and charge transfer at the metal/semiconductor interface. We performed first-principles density functional calculations to study the energetics and electronic structures of Pb/Si(111) at different Pb coverages. We identified atomic models and domain wall arrangement for the controversial dense (coverage ~4/3 ML) Pb/Si(111)-R3xR3 phase observed in STM experiments.

Program Impact:
Our proposal of mixed SiGe addimer on Si(001) allowed the analysis of experimental STM data to understand the kinetics of initial growth when Ge is deposited on Si(001). Our results on the various adatom and addimer diffusion on Si(001) surface provide a most accurate and detailed picture about the atomic process at the the initial stage of epitaxial growth of Si and Ge on Si(001). The simulation study of laser ablation on diamond surface suggested an efficient way for better diamond surface processing.

Interactions:
Internal- M. Tringides (Ames Lab), P. Molian (ISU-Mechanical Engineering)
External- U. of Wisconsin, (M. G. Lagally), Brown University (C. Ciobanu and V. Shenoy)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Three invited talks, 10 papers

Personnel Commitments for FY2002 to Nearest +/- 10%:
C. Z. Wang (10%), K. M. Ho (12%), Students and visiting scientists: Wencai Lu (30%), Mingsheng Tang (10%), Tzu-Lian Chan (100%), Feng-Chuan Chuang (60%), Mehmet Su (50%), Byeong Min (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $116k **FY01 BA $**129k **FY02 BA $**134k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP:
Superconductivity Theory

FWP Number: AL-90-540-003

Program Scope:
The objective of this program is to develop theoretical understanding of the properties of superconductors in magnetic fields. We have studied the critical fields, critical currents, ac losses, and the structure and dynamics of vortices and vortex lattices. We have focused much of our attention on the effects of strong anisotropy in the high-temperature cuprate superconductors and two-gap behavior in MgB_2.

Major Program Achievements (over duration of support):
* Developed theory of two-dimensional pancake vortices in samples of finite thickness and applied this to experiments in layered superconductors containing crossing Josephson-vortex lattices.
* Developed theory for the combined effect of geometrical barriers and bulk pinning on the field-dependent critical current in type-II superconducting strips.
* Writing editorials for the *High-T_c Update* web site, highlighting high-temperature superconductors and MgB_2.
* Using nonlocal London equations, developed theory for vortex-lattice transitions in superconducting borocarbides.
* Using a two-gap model, developed a theory predicting different temperature-dependent anisotropies for the upper critical field and the London penetration depth in MgB_2.
* Developed general theory for torque acting on anisotropic superconductors in magnetic field and applied it to the two-gap superconductor MgB_2.

Program impact:
* New low-noise 77 K SQUIDs are currently being fabricated worldwide following our theoretical predictions that, in the earth's magnetic field, vortices are not trapped in superconducting lines of width less than about 5 μm.
* The *High-T_c Update* web site is widely read, currently receiving approximately 40,000 hits per month.
* Small-angle neutron scattering, scanning tunneling microscopy, and decoration experiments in superconducting borocarbides have confirmed our predictions of vortex-lattice transitions.

Interactions:
* Internal: P. C. Canfield, D. C. Johnston, and D. K. Finnemore.
* External: Bell Laboratories, IBM, Stanford University, University of Wisconsin (Madison), University of Maryland, Los Alamos National Laboratory, National Institute of Advanced Industrial Science and Technology (Tsukuba, Japan), Okayama University (Japan), Isfahan University of Technology (Iran), UAE University (United Arab Emirates), Nizhny Novgorod University (Russia), Institute of Solid State Physics (Moscow, Russia), University of Bath (UK), University of Geneva (Switzerland), and Tel Aviv University (Israel).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
* VGK was named a Fellow of the American Physical Society (March 2000).
* JRC is founding editor of AIP and APS'S *Virtual Journal of Applications of Superconductivity* (August 2001) and was named to the editorial boards of *Physical Review B* and *Superconductor Science and Technology.* Fellow of the APS.

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. R. Clem (25%), V. G. Kogan (100%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $199k **FY01 BA** $230k **FY02 BA** $240k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Theory
Electronic and Structural Properties of Solids and Clusters

FWP Number:AL-90-540-003

Program Scope: The study of fundamental interactions in materials through first-principles quantum mechanical calculations and atomistic simulations. Current efforts focus on the development of accurate and transferable environment-dependent tight-binding potentials for material simulations requiring hundreds to thousands of atoms. The study of the behavior of various atomic clusters allow us to test our potentials in very different environments in addition to discovering the novel structures and properties of nano-scale objects.

Major Program Achievements (over duration of support):
Develop Environment-Dependent Minimal-Basis-Set Atomic Orbitals: In collaboration with Ruedenberg's group in chemistry, we have recently developed a method to extract environment-dependent minimal-basis-set orbitals from ab initio wavefunctions. These orbitals give an exact description of the occupied electronic states and are highly localized on the individual atoms, making them ideal for use in an accurate tight-binding description of the system. This scheme is easily generalizable to systems involving different atomic species and will simplify the task of generating accurate tight-binding potentials for complex systems.
Applications of tight-binding molecular dynamics: 1.) Using an accurate environment-dependent potential for Mo, we have predicted successfully the reconstruction of the Mo(001) surface and the core structure of the (111) screw dislocation in bcc Mo. 2.) Following up on our earlier success in studying the geometries and properties of carbon clusters, we have developed an efficient genetic algorithm to study the geometry of atomic clusters. Applications to silicon, germanium and tin clusters were successful in locating the global energy minimum for clusters with sizes up to about 20 atoms. Our work, in collaboration with mobility experiments (Northwestern University), photoelectron measurements (Germany), firmly established the tricapped trigonal prism packing as the structural motif of teen-sized Si, Ge, and Sn clusters. This motif is unique to these species and the results explained the abnormal properties of these clusters, including their inverted binding energy size-dependence and fission fragmentation behavior. We are extending these studies to atomic clusters with more than one type of atom: Si-H, C-H and Si-O systems. 3.) An important area of application for our TB potentials is the study of adatom and addimer diffusion and intermixing on semiconductor surfaces and the behavior of stepped surfaces (see Tringides' section)

Program Impact:
The tight-binding molecular dynamics pioneered by our group has been adopted by many research groups worldwide for material simulations of systems which are too complicated or time-consuming to be studied with traditional first-principles density-functional techniques. We expect the new potential generating method will also be quickly picked up and disseminated once thoroughly tested and released.

Interactions:
Internal- Ames Lab Chemistry (K. Ruedenberg, M. Gordon, M. Schmidt)
External - Northwestern University (M. F. Jarrold, A. A. Shvartsburg), University of Minnesota: Chemical Engineering (J. R. Chelikowsky), MIT: Nuclear Engineering (J. Li and S. Yip),

Recognition:
Two invited talks, 7 papers published. This work was awarded the Materials Science Award for Sustained Outstanding Research in Solid State Physics (before this funding period). Ho is an APS Fellow.

Personnel:
C. Z. Wang (70%), K. M. Ho(10%), students: Feng-Cuan Chuang (20%), Jun Liu (10%), David Lastine (20%), Mehmet Su (10%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$100k **FY01 BA** \$95k **FY02 BA** \$90k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics - Theory
Strongly correlated systems

FWP Number: AL-90-540-003

Program Scope:
The development and application of modern approaches in many body theory to experiments on novel materials including hard condensed matter systems like high temperature superconductors, organic conductors, heavy fermion systems, and nearly magnetic systems as well as soft condensed matter systems like micro-emulsions and physical gels. Emphasis is given to the prediction or description of new physical effects and materials properties caused by the competition between strong interactions and disorder, interactions on different length scales, etc. using, for example, energy landscape approaches or the concept of quantum criticality

Major Program Achievements (over duration of support):
Developed a new theory for magnetic quantum phase transitions in metals with disorder and defects. In nearly magnetically ordered metals, quantum tunneling of rare ordered droplets is dramatically suppressed, leading to super-paramagnetic behavior with important implications for theories of non-fermi-liquid behavior in heavy fermion materials.
Predicted self generated glassiness in classical and quantum systems with micro-phase separation with wide applications to strongly correlated transition metal oxides, metal ammonia mixtures, micro-emulsions of oil-water-amphiphiles, block-copolymers, and physically associated gels, where specific calculations for all these systems have been performed.
Developed a new dynamical mean field theory for glasses with application to structural and metallic glasses.
Development of the spin fluctuation model for d-wave superconductivity with "Fingerprints" of a spin mediated pairing state (chiefly associated with the emergence of the neutron resonance peak in the spin response in a d-wave superconductor) were proposed and identified in spectroscopic experiments on optimally doped cuprate superconductors.

Program impact:
Our first demonstration of a new self-generated electronic glass state in a correlated material motivated experimental verification and theoretical generalization by various groups world wide.

Interactions:
Internal- Ames Lab.: Condensed Matter (M. Tringides, P. Canfield), Chemistry (X. Song), Metallurgy and Ceramics (J. Morris).
External- LANL (D. Pines, A. Bishop, A. Saxena); UCSD (P. G. Wolynes), Columbia Univ. (A. J. Millis); Univ. of Wisconsin Madison (A. Chubukov), Univ. of Illinois at Urbana-Champaign (P. Goldbart), University of Illinois at Chicago (D. K. Morr), Cambridge University (M. Turlakov).

Recognitions, Honors and Awards (at least partly due to support under this FWP or subtask):
Research Innovation Award of the Research Corporation (2001).
15 invited talks at major international conferences.

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. Schmalian (PI-30%)
E. Hankiewicz (postdoc, 100%)
Sangwook Wu (student-19%), Jun Liu (student-6%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$100k **FY01 BA** \$110k **FY02 BA** \$125k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Spin Dynamics

FWP Number: AL-90-540-003

Program Scope:
Create, develop, and use first principles methods that will allow accurate simulations at the atomistic level of complex realistic magnetic materials. We partner with ORNL scientists in implementing these methods on modern supercomputers to allow treatment of large unit cells (up to 3000 atoms) so that the thermal and other dynamical properties can be simulated.

Major Program Achievements (over duration of support):
Achieved the first consistent explanation of the nature of hysteretic phenomena in the CoPt family of magnets. A practical combination of first-principles, micromagnetic and microstructural was used. We predicted two sources of coercivity in polytwinned CoPt type magnets developing at different length scales: domain wall pinning at antiphase boundaries and splitting at twin boundaries. We developed an approach for self-consistent calculations of the many-body Green function in transition metals and insulators. Reasonable agreement with experimental results is obtained. The technique can be considered as an ab-initio alternative to both the LDA and LDA+U methods with much wider range of applicability for correlated systems. A new general technique for the calculation of the exchange coupling parameters and spin wave spectrum suitable for non-local and full-potential technique was developed. A general coarse graining scheme was developed to couple the atomistic spins near defects to the average "spins" used in micromagnetics in regions far from the defects. Simulation methods were also developed to follow quantum spin oscillations in quantum dots and in magnetic molecules when those systems are subjected to the decoherence effects caused by a thermal spin bath of surrounding nuclear spins.

Program Impact:
Our development of first principles spin dynamics (and our treatment of non-collinear magnetism in general) has been widely disseminated, although for large systems the simulation of the thermal fluctuations in large unit cells is still very demanding and requires considerable supercomputing resources. The development of bridging length scale methods is gaining attention as more groups specializing in micromagnetics are looking into methods to incorporate the accurate first principles information about magnetic interactions near defects, interfaces, and surfaces. The studies on spin bath decoherence have implications for the feasibility of implementing quantum computing using real materials.

Interactions:
Internal- F. Borsa (NMR on magnetic systems), R. McCallum (Met. and Cer.), C. Stassis (neutrons).
External- M. Stocks (ORNL), A. Lichtenstein (Nijmegen, The Netherlands)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
This project is one of the DOE Science 100 accomplishments (for first 25 years of DOE). The participants average 6 invited talks per year per PI. Harmon is a Fellow of the American Physical Society and has helped organize focused sessions at two March meetings and an invited symposium at the MMM conference. He was on the organizing and program committee for an international conference on computational magnetism held at Gerorgetown Univeristy in July 2002, and he is a founding steering committee member of the Computational Materials Sciences Network, and Associate Editor for the Journal of Phase Equilibria. He is also serving on the Executive Committee of the Division of Condensed Matter Physics of the American Physical Society.

Personnel Commitments for FY2002 to Nearest +/-10%:
V. Antropov (PI-70%), B. Harmon (PI-10%), V. Dobrovitski (50%), K. Belachtchenko (PD-100%), N. Zein (Visting Scientist-20%), M. Katsnelson (Visiting Scientist-20%), M. Al-Saqer (student-50%).

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $481k **FY01 BA** $450k **FY02 BA** $450k
(Note: Approximately $150k/year is sent to ORNL as a reconciling transfer for work on this project)

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory
Left –Handed Materials

FWP Number: AL-90-540-003

Program Scope:
Left-handed materials (LHMs) are composite materials with novel and unique electromagnetic (EM) properties, which are not determined by the fundamental physical properties of their constituents but by the shape and the distribution of specific patterned included inclusions. LHMs have the unique property of having both the effective permittivity and the effective permeability negative over some frequency range. The scope of the program is the theoretical understanding, analysis, development and testing of LHMs, and also the investigation of their feasibility for potential applications.

Major Program Achievements (over duration of support):
Developed new transfer matrix codes for LHMs. The transmission, reflection and absorption were calculated for realistic LH structures and were compared with experiments (done at UCSD and Bilkent Univ.). The dependence of the transmission properties of LHMs on the real and imaginary part of the permittivity of the metal, the length of the system and the size of the unit cell were obtained. New LHMs structures were designed and their transmission properties were experimentally measured.

By analyzing the reflection and transmission coefficients, calculated from transfer matrix simulations on finite lengths of LHMs, the effective permittivity and permeability of LHMs were determined. A frequency region was obtained where both the permittivity and the permeability were negative with negligible imaginary parts. In this negative region, the index of refraction *n* was found to be unambiguously negative. While we utilize simulation data in this study, the technique we describe will be readily applicable to the experimental characterization of experimental LHMs whenever the scattering parameters are known.

Program impact:
Provided the first transfer matrix and FDTD calculations of LHMs. This will eventually lead to LHMs with improved transmission properties. The technique developed in obtaining the effective permittivity and other groups will use permeability of LHMs from refraction and transmission coefficients widely.

Interactions:
External - E. Ozbay, Bilkent University, Turkey; D. Smith and S. Schultz, UCSD; Boeing's Phantom Works, Seattle; Research Center of Crete; and J. Pendry, Imperial College.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of **AAAS**, 2002 Senior Alexander von Humboldt Award, 2002
Invited Talks: NATO ASI on *Wave Scattering in Complex Media: From Theory to Applications*, Cargese, Corsica, France, June 2002; 3rd WE-Heraeus Summer School on *Photonic Crystals: Optical Materials for the 21st Century*, Lutherstadt Wittenberg, Germany, July 2002; *Photonic Crystals Down Under*, The Australian National University, Canberra, Australia, August 2002;International Workshop on *Photonic and Electromagnetic Crystal Structures, (PECS-IV),* Los Angles, CA, USA, October 2002.

Personnel Commitments for FY2002 to nearest +/- 10%:
Soukoulis (5%), Rousochatzakis (PD-100%), Peter Markos (Visiting Scientist-20%), Unpaid associates: E. N. Economou, E. Ozbay, Tom Lloyd, R. Moussa, G. Tuttle.

Authorized Budget (BA) for FY00, FY01, FY02: (New program, will be full in FY03)
FY00 BA $ **FY01 BA $** **FY02 BA** $50k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Computational Materials Sciences Network – Magnetism Project / Ames Laboratory

FWP Number: AL-90-540-003

Program Scope:
The Computational Materials Sciences Network (CMSN) is a virtual center consisting of scientists interested in working together, across organizational and disciplinary boundaries, to formulate and pursue projects that reflect challenging and relevant computational research in the materials sciences. The projects appropriate for this center involve those problems best pursued through broad cooperative efforts, rather than those key problems best tackled by single investigator groups. CMSN operates similarly to the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials, coordinated by George Samara at Sandia. As in the Synthesis and Processing Center, the intent of the modest funding for CMSN is to foster partnering and collective activities.
This particular CMSN project is titled: "Magnetic Materials – Bridging Basic and Applied Science". It involves scientists from ORNL and several universities (Florida State, Alabama, Georgia, Illinois, and UC-Irvine). While the underlying mechanisms responsible for the magnetism of materials involve electronic interactions at the atomic levelk the bulk properties of permanent magnets are governed at a larger length scale and are greatly influenced by microstructure. This project brings together experts all various length scales. The subtasks are: 1)Fundamental Physics, 2) First Principle derived parameters, 3) Domain Walls, 4) Coarse Graining, and 5) Micro-magnetics.

Major Program Achievements (over duration of support):
Ames Lab scientists have made significant contributions on new techniques (spin dynamics), first principle derived parameters (methods to obtain exchange and anisotropy parameters). They have developed a new coarse graining technique which is accurate for dynamical processes, and they have derived domain wall pinning parameters for anti-phase boundary and twin boundary interfaces for CoPt. These results are being shared with other members of the team for development of a general micromagnetics codes and for testing the techniques using large system classical spin dynamics simulations.

Program Impact:
The creation of CMSN, and this magnetic properties team has led to collaborations among groups which would not otherwise have come together to solve issues with atomic interactions affecting practical bulk magnetic properties. The problems are enormous and well beyond the means of any one group or laboratory. The response to the Earth Simulator for materials science is most strongly motivated by CMSN like teams, particularly the one in magnetism, where supercomputing is essential and the problems are recognized as important for science and technology.

Interactions:
External-Members of the CMSN magnetism team include:, G. Brown (Florida State), Duane Johnson (Illinois), David Landau (Georgia), Per Rietveld (Florida State), Renat Sabrianov (Nebraska,Omaha), T. Schultess (ORNL), M. Stocks (ORNL), P. Vischer (Alabama)), Ruqian. Wu (UC-Irvine).

Recognitions, Honors and Awards (attributable to support under this FWP or subtask):
This team is responsible for organizing focused sessions at two March meetings and an invited symposium at the MMM conference. The team organized an international conference on computational magnetism (ESCM2002) held at Gerorgetown Univeristy in July. Harmon organized a Pan American Advanced Studies Institute (funded by NSF) on Computational Materials Science, which was held in Santiago Chile in 2001, with "Bridging Length Scales in Magnetism" as a series of lectures by a team member (Stocks).

Personnel Commitments for FY2002 to Nearest +/-10%:
B. Harmon (PI-unpaid), V. Antropov (unpaid), V. Dobrovitski (50%).

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $120k **FY01 BA $**120k **FY02 BA $**110k
(Note: Money from Ames Lab is used to contract out to the University partners, for travel, and to pay half a post doc; money for the other team participants goes through ORNL.)

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: The program seeks to expand our knowledge and understanding of solid state chemistry, particularly of polar intermetallic compounds and salts of the active, transition, and post-transition metals via high quality exploratory syntheses in Ta, Nb containers, structural studies, bonding, and physical properties of novel discoveries. Prominent are wide-spread interstitial chemistries, phases near valence (Zintl) formulations, cluster and network structures, and their electron localization (or not) and bonding.

Major Program Achievements (over duration of support):
Explored, developed and organized a new field of polar intermetallics formed between active metals and the triels (Ga, In, Tl), discovering much new chemistry beyond the classical Zintl (valence) boundary.
Discovered numerous phases stabilized by hydrogen, especially for Cr_5B_3- and Mn_5Si_3-type hosts of with tetrels (Si–Pb) and triels (Ga–Tl). Nearly all of these had been erroneously reported as binary compounds.
Syntheses and characterization of new Zintl (valence) compounds: e.g. Ca_{2-x} Mg_xTt (Tt=Ge, Si), $Yb_{36}Sn_{23}$, K_2Ga_3, Ba_6Ga_{25-x}, $K_6Tl_2Sb_3$, $Na_{10}(Ga_{10}Ni)$, K_5InPb_8. Systematics of Zintl phases via property data.
New unprecedented thallium cluster anions: (a) the Pd-centered $T1_{11}^{7-}$ in $K_8(Tl_{11}Pd)$, (b) Cd-centered confacial pentagonal antiprismatic chains of Tl in $Cs_5Cd_2Tl_{11}$, (c) pentagonal bypyramidal clusters in $K_{10}Tl_7$, (d) tetrahedral stars in K_6Tl_{17}. All are metallic. The square pyramidal anions in the isostructural La_3In_5, La_3Sn_5, Sr_3Sn_5, Ba_3Pb_5 are related.
Discovery and definition of new hyperelectronic network structures of metals with indium and thallium: $SrIn_4$, Sr_3In_5, K_2SrIn_7, $BaTl_3$ with a relatively low number of cations.
Discovery of principles of stabilizing new cluster and network anions through use of mixed cation sizes.
Oxidative substitution of gold and silver in the valence-precise gallium networks to give new structures.

Program Impact:
Our discoveries have impacted or motivated solid state chemistry concepts and programs around the world and have correspondingly attracted students from many places. Invited talks elsewhere since 1999 total 27.

Interactions:
Iowa State University: Materials Chemistry (G. Miller); Condensed Matter Physics (P. Canfield)
Metallurgy & Ceramics (M. Kramer, K. Gschneidner);
U.S. Universities: Notre Dame, Houston, Northwestern, Michigan State, Utah State, Texas A&M;
Non-U.S. Universities: Max-Planck Institute, Stuttgart; NRIM, Japan; LGChem, Korea; FIRSM, Fuzhou, China, and Universities at Barcelona (Spain), Cologne, Darmstadt (Germany), Montpellier (France);
U.S. National Laboratories: PNNL, ANL

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
National Academy Sciences; Fellow, AAAS; 2 American Chemical Society National Awards; John C. Bailar Jr. Medal in Inorganic Chemistry; Midwest and Iowa (ACS) Awards; 2 DOE Awards in Materials Chemistry; A.v. Humboldt Sr. Scientist Award; 5 Special Lectures.

Personnel Commitments for FY2002 to Nearest +/- 10%:
John D. Corbett (group leader, 25%), S. Liu (70%), B. Lin (100%), A. Mudring (A.v. Humboldt Fellow, 40%), A. Yang (25%), S. Standley (20%), G. Tobias (10%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $378,600 **FY01 BA $**368,000 **FY02 BA $**356,500

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: We study the crystalline solids that form at high temperatures, usually in the range between 1399 and 2000 K. We have found that new compounds and new structures for old compounds frequently form in systems involving metal-metal bonding when they are studied in this temperature range. The materials, as well as being of intrinsic chemical interest, are of future practical interest because they form as stable compounds in system at these high temperatures. The understanding of the chemistry that occurs in materials processing and energy conversion in future high-temperature applications will require an understanding of reactions that may have either a positive of negative impact on the application, and this understanding will depend in an essential way upon a knowledge of the solids, and types of solids, that are stable in the high-temperature systems

Major Program Achievements (over duration of support):
High-temperature modification of Y_5Sb_3 and its ternary analogue $Y_5Ni_xSb_{3-x}$. The structure of $Y_5Ni_xSb_{3-x}$ ($0 \leq x < 1$) is stabilized at high temperatures by the configurational entropy, resulting from a statistical mixture of Sb and Ni atoms on one site.

The structure of $RECuAs_{2-x}P_x$ compounds depends on the composition: introducing more phosphorus results in the distortion of the originally tetragonal lattice of the arsenides. Symmetry-breaking transitions go through the orthorhombic lattice in the arsenophosphides to different types of the lattice in the phosphides. If the temperature dependence of the structures for many compounds is well studied, this project represents the most extensive insight into the compositional dependence of the structures of the ternary compounds.

Program Impact:
Our work has led the way in the study of metal-rich systems, especially those stable at high-temperatures. Our program is well known in the U.S., Europe and Asia, and there are groups on all three continents carrying out research of the type that had it's genesis in our group.

Interactions:
Iowa State University: Materials Chemistry (G. Miller, J. Corbett)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
None

Personnel Commitments for FY2002 to Nearest +/- 10%:
H.F. Franzen (group leader, 0%), Y. Mozharivskij (100%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $118,700 **FY01 BA $**61,200 **FY02 BA $**59,000

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: The goals of this project are: (1) To elucidate where the atoms are located in quasicrystals. Ideas will be formulated from crystalline approximants and other crystal structures in the same or similar chemical system where quasicrystals occur; (2) To develop a theoretical underpinning for the concept of "magic numbers of electrons," that exists among known quasicrystals, i.e., to establish a "Hume-Rothery" or "Zintl-Klemm" approach towards the "prediction" of new quasicrystalline materials; (3) To use theory to extract an interpretation of the physical and chemical properties of quasicrystalline phases, in particular, related to the distribution of elements in these intermetallic structures.

Major Program Achievements (over duration of support):
New quaternary approximants in the Li-Mg-Zn-Al system. Our observations did lead to an understanding of the local electronic structure and the atomic distribution in the Bergman Mg-Zn-Al phases. Li can completely substitute for Mg, and the Zn/Al ratio changes to keep the total valence electron concentration in a narrow range between 2.0 and 2.2 electrons per atom.
A magic electron count in the bergman cluster. We developed a model based on tight-binding theory and have shown that the atomic framework is mostly dictated by minimizing the bond energy term, whereas the decoration pattern of different elements depends on the site energy term. In the Bergman structures, the bond energy term reaches its lowest value for 2.20 electrons per atom, which is in excellent agreement with our own experiments in the Li-Mg-Zn-Al system.
A new quasicrystalline approximant. A new structure was discovered that is built up of sheets that show pentagonal bipyramidal building units: $Li_{10}Mg_6Zn_{31}Al_3$. There is a close analogy between this new structure and the Bergman phases and possible relations to decagonal quasicrystals.
Approximants and quasicrystals in Ga-systems. We have carried out the first thorough synthesis and characterization of GaM (M = Cr, Mn, Fe), which are a new class of approximants for "Mackay"-based quasicrystals. Reactions in Ga-Mn-Pd led to a different crystalline approximant; Ga-Mn-Pd-Ru show a quasicrystal whose structure is under investigation.
Linking quasicrystals with incommensurate structures. Exploration in the binary Pd-Zn system is revealing structures built up of Zn icosahedra surrounded by complex Pd polyhedra that follow different length scales in a single (stacking) direction. By varying the composition, it is possible to achieve different combinations of length scales with our goal to identify a Fibonacci series.

Program Impact:
Through experimental and theoretical efforts, we feel that our efforts are building a "molecular-based" understanding of quasicrystalline approximant structures, and hope this effort will lead to rational targets of new quasicrystals.

Interactions:
Iowa State University: Metallurgy and Ceramics (K. Gschneidner, V. Pecharsky); Non-U.S. Universities: ETH-Zürich, Switzerland; U.S. National Laboratories: ANL, LANL (Neutron diffraction)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Visiting Scientist, ETH-Zürich; 5 Invited talks

Personnel Commitments for FY2002 to Nearest +/- 10%:
G.J. Miller (group leader, 0%), O. Gourdon (90%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $49,700 **FY01 BA** $70,800 **FY02 BA** $48,500

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:

Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: One task is to investigate the interstitial chemistry of transition metal silicides of the $A_5Si_3Z_x$ type and to determine the influence of the interstitial atoms on the chemical, thermal, and mechanical properties. Another task is to synthesize and control the architecture of pillared structures of ceramic materials. In a case study of α-Ni(OH)$_2$, homogeneous precipitation is used to produce α-Ni(OH)$_2$ and to stabilize the structure by controlling the formation of intercalating ions (atomic pillars).

Major Program Achievements (over duration of support):
Small atom additions to Ti_5Si_3 occupy Z interstitial sites (Z=B,C,N,O), and their bonding with the surrounding Ti2 atoms is associated with the decrease in the anisotropic properties of Ti_5Si_3.

The LMTO (linear muffin tin orbital) method was used to calculate equilibrium structural parameters for $Ti_5Si_3Z_x$ (in collaboration with K. M. Ho of Condensed Matter Physics). Estimated parameters agree with experimental findings and suggest the stabilizing effect of the interstitial dopants in the Mn_5Si_3 structure.

The oxidation resistance of C-doped Ti_5Si_3 is improved by 1000 times at 1000°C in air compared to undoped Ti_5Si_3. The accelerated oxidation of non-carbon doped material is controlled by the inward diffusion of nitrogen and subsequent subscale formation of phases from the Ti-Si-N-O equilibrium.

Homogeneous precipitation of Ni^{+2} in aqueous solution with urea produces phase-pure α-Ni(OH)$_2$ with significant OCN^- intercalating between the Ni(OH)$_2$ layers. The growth mechanism is the aggregation of 9 nm primary crystallites to form 2 μm particles.

Co substitutions for Ni act as an atomic anchor to carbonate and/or OCN^- ion pillars, increasing the spacing between the plate-like structure of nickel hydroxide. These pillars are expected to enhance exchange of ions and solvent molecules during the electrochemical cycling process.

A predictive model using kinetic simulation was developed and accurately predicts the experimentally observed particle formation.

Program Impact:
Improving the oxidation resistance of doped silicides by interstitial modification has led to a renewed interest of these materials within the research community. Mo_5Si_3B materials are now prime candidates for high temperature structural applications in severe environments.

Interactions:
Iowa State University: Materials Chemistry (J. Corbett, G. Miller); Metallurgy & Ceramics (M. Kramer, B. Cook, D. Sordelet, D. Rehbein, D. Bernard); Center for Nondestructive Evaluation (J. Gray)
U.S. National Labs: Ames, ANL, INEL, LANL, ORNL; Industrial: C.M. Furnaces, I^2R Element Co.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Four U.S. Patents have been issued for the use of these doped silicide materials in engineering applications
Invited presentations: 15
Nominations for Significant Implication for DOE Related Technologies (1998)

Personnel Commitments for FY2002 to Nearest +/- 10%:
M. Akinc (group leader, 10%), A. Thom (60%), V. Behrani (50%), B. Mavis (10%), Y. Sui (40%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $183,100 **FY01 BA $**225,000 **FY02 BA $**214,000

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: The objectives are to design, synthesize, characterize, process and study novel organometallic (especially Group 14) materials that have promising properties for use in ceramic, composite and optoelectronic applications. Current effort is on materials which are thermally converted to ceramics, conjugated organic monomers and polymers, and detailed studies on the thermal and photochemical rearrangements and decompositions of model systems.

Major Program Achievements (over duration of support):
Discovery of both thermal and photochemical additions of Si−Si bonds to carbon−carbon triple bonds. These reactions, some of which are apparent violations of the Woodward-Hoffmann Rules, only occur in an intramolecular fashion. Systems have been designed to exploit this novel chemistry by preparing silicon-bridged trans-stilbenes locked in polycyclic structures and possessing attractive optical properties.
Kinetic and mechanistic analysis of the thermal decomposition of organogermanium compounds.

Synthesis of unique, highly strained cyclicsilaacetylenes, e.g., 1,2,3,4-tetrasilacyclohexyne.

Complete mechanistic, kinetic and theoretical analysis of thermally-induced isomerization of olefins to carbenes via 1,2-silyl migration on vinyl silanes.

Program Impact:
Fundamental studies of the detailed mechanisms of thermal decompositions of appropriate model systems can allow the rational design of efficient preceramic polymeric materials. Also, our synthetic efforts in optoelectronic materials are an integral part of a larger team effort in this arena.

Interactions:
Iowa State University: Condensed Matter Physics (J. Shinar)
Metallurgy and Ceramics (O. Unal, I. Anderson)
Chemical Sciences (M. Gordon)
U.S. Universities: Univ. of Utah, Univ. of Arizona
U.S. National Laboratories: LANL

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Frederic Stanley Kipping Award (ACS) in Organosilicon Chemistry (1982)
DOE/BES Outstanding Scientific Accomlishment in Materials Chemistry (1989)
American Chemical Society, Midwest Award, 1995

Personnel Commitments for FY2002 to Nearest +/- 10%:
T.J. Barton (group leader, 0%), Andrew Chubb (50%), Nathan Classen (50%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $210,500 **FY01 BA $**115,200 **FY02 BA $**73,700

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: The principal objective of this program is the synthesis and characterization of biomimetic self assembling poly(ethylene glycol) (PEG)-based block and graft copolymers with cationic functionalities. These copolymers exhibit very unique behavior, specifically self assembly into nanoscale micelles and thermoreversible macroscale gels coupled with pH sensitive swelling/syneresis. While the main objective is to obtain a fundamental understanding of the phase behavior of these systems, these polymers are excellent candidates for self-regulated drug delivery and gene therapy devices. These polymers form complexes with DNA and studies will be carried out to understand the interactions and transport of these complexes across lipid bilayers that mimic cell membranes. We have developed some novel synthetic routes to synthesize triblock and pentablock copolymers of PEG with cationic copolymers and are investigating the micellization and gelation behavior of these polymers.

Major Program Achievements (over duration of support):
PEG-PDEAEM synthesis. We have developed novel synthetic routes to link blocks of PEG and anionically polymerized poly(diethylaminoethylmethacrylate) (PDEAEM), a cationic polymer, to form block copolymers.

PDEAEM-PEG-PPO-PEO-PDEAEM synthesis. We have also developed techniques to develop these new pentablock copolymers listed above. These impart additional hydrophobicity to the copolymer and these polymers undergo temperature sensitive micellization and gel formation.

Copolymer characterization. We have characterized the self assembly of these copolymers and studied their phase behavior using a variety of techniques such as gel permeation chromatography, cryo-TEM, FTIR, NMR, differential scanning calorimetry, and light scattering.

Interactions with biomolecules. We have conducted investigations on the interactions of these polymers with biomolecules at various pH ranges to test their pH sensitivity. We have also investigated the efficacy of these polymers in delivering DNA to cells in culture.

Program Impact:
Our research results have helped generate a renewed focus on these novel self-assembling nanoscale water soluble, pH sensitive block copolymers with unique thermogelling charcateristics. The impact is reflected in the number of invited talks and literature citations.

Interactions:
Iowa State University: Materials Chemistry (V. Sheares, K. Schmidt-Rohr)
U.S. Universities: Drake University

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2 NSF CAREER awards, 2 ISU Foundation Early Excellence in Research awards, MIT's Technology Review magazine's "Top 100 Young Innovator" award
10 Invited talks

Personnel Commitments for FY2002 to Nearest +/- 10%:
S. K. Mallapragada (group leader, 0%), B. Anderson (40%), S. Cox (20%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $0 **FY01 BA** $21,400 **FY02 BA** $47,200

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: The primary objective of this research is the evaluation of catalytic benefits of Lewis acid sites in surfaces of metal oxide electrodes for anodic transfer of O-atoms from H_2O to the oxidation product(s). This work is based on the premise that the mechanism involves discharge of H_2O to generate OH radicals adsorbed at the anode surfaces followed by anodic transfer of O-atoms from the OH species to adsorbed reactant molecules. Electrodes include PbO_2 films doped with altervalent metallic sites, e.g., Bi(V) and Fe(III). A secondary objective is determination whether there is a cathodic analog by which O-atoms on reactant species can be converted to H_2O during reductive processes. The reactant of interest is the nitrate anion (NO_3^-) and electrodes being studied include Cu that is alloyed by metals having lower d-orbital occupancy.

Major Program Achievements (over duration of support):
Demonstrated catalytic benefit of low levels of Fe(III) sites in PbO_2-film anodes to increase current efficiency for anodic (oxidative) conversion of waste aromatic compounds to CO_2.

Demonstrated benefit of simultaneous uv illumination of metal oxide anodes during anodic degradation of aromatic compounds with CO_2 as a major product.

Program Impact:
The fundamental benefit of this research is an increased understanding of the catalytic role of Lewis acid sites in electrode surfaces utilized to achieve various electrolytic processes. Immediate commercial impact is expected to come from: (i) degradation of toxic organic wastes generated in pesticide research labs using small electrolysis systems; (ii) conversion of HNO_3 wastes to NH_2OH for possible use as a fuel in rocket propulsion; and (iii) discovery of new electrode materials for use as amperometric sensors applied to liquid chromatography and flow-injection analysis.

Interactions:
U.S. Universities/Colleges: James Cox, Miami University, Oxford, OH
Non-U.S. Universities: Ch. Comninellis, Institut de Genie Chimique, Lausanne, Switzerland
U.S. Industries: Dionex Corp., Sunnyvale, CA; Electrosynthesis Co., Inc., Lancaster, NY;
Lynntech, Inc., College Station, TX

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Charles N. Reilly Award
1 Invited talk

Personnel Commitments for FY2002 to Nearest +/- 10%:
D. C. Johnson (group leader, 10%), B. Simpson (40%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $127,600 **FY01 BA $**95,700 **FY02 BA $**46,900

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: Step growth polymers represent an important class of high-technology materials, for which the tailoring of polymer structures to give a specific set of properties is the essential chemical art. Previously, we have described the simple synthesis of soluble poly(*p*-phenylene)s via nickel coupling chemistry. In the present work, we extend this chemistry to access a number of important derivatives via a novel, post-polymerization reaction. This chemistry addresses the issue of how one introduces useful functional groups, not tolerated by the nickel polymerization catalyst, into these materials.

In addition to synthetic alterations, a second alternative to tailor-make these materials is to use additives. Previously, we ascertained that the inherent quasicrystal properties (low thermal conductivity, excellent scratch resistance, high softening temperatures, and low coefficients of friction) are manifested in the polymeric composites. The purpose of the present work is to exploit the low wear, low abrasion properties and examine these materials in biological applications, such as in joint replacements.

Major Program Achievements (over duration of support):

A new methodology for poly(paraphenylene) synthesis developed. Using this versatile methodology, based on nucleophilic aromatic substitution, many new functionalized, high performance polymers have been efficiently made from a single precursor.
New polymer/quasicrystal composites fabricated. Thermoplastic and thermoset composites have proven to outperform hard, binary compound-filled materials (such as iron aluminide) in wear tests; The composites have a unique combination of wear resistance while not being abrasive; Initial tests using commodity plastics (polystyrene, polyethylene, etc.) show improved wear properties comparable to the filled high performance polymer matrices.

Program Impact:
Our research in high performance polymers has opened the door to functionalized materials that could not otherwise be accessed. The applications are in polymeric membranes, insulating and nonlinear optical materials. The impact of the quasicrystal work can be seen in the significant industrial and academic interest and in the number of invited lectures and publications describing the work.

Interactions:
Iowa State University: Materials Chemistry (S. Mallapragada, J. Anderegg); Metallurgy and Ceramics (D. Sordelet); Dept. of Materials Science and Engineering (J. Otaigbe); Ames Laboratory (C. Jenks)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Honored by the American Chemical Society as one of the top 12 young female chemists in the country (2002)
Iowa State University, College of Liberal Arts and Sciences Master Teacher (2001)
Iowa State University Teacher of the Year, College of Liberal Arts and Sciences (2001)
3M Young Faculty Award (2001)
Early Excellence in Research Award, Iowa State University (2000)
7 invited lectures last year, including national and international conferences

Personnel Commitments for FY2002 to Nearest +/- 10%:
V.V. Sheares (group leader, 0%), K.G. Baikerikar (25%), E. Hagberg (20%), Y. Yang (30%),

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $74,400 **FY01 BA** $120,400 **FY02 BA** $100,100

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: We develop and apply advanced solid-state nuclear magnetic resonance (NMR) methods to elucidate the nanometer-scale structure and dynamics of heterogeneous polymer materials. Specifically, we are studying intercalated and exfoliated polymer-clay nanocomposites; perfluorinated ionomers as used, for instance, in all-solid H_2/O_2 fuel cells; and the complex nanometer-scale phase structure in semicrystalline polymers after plastic deformation.

Major Program Achievements (over duration of support):
High-sensitivity ^{2}H NMR. We have developed the PRIDE (proton inverse detected deuteron) NMR technique, which provides a ~15-fold sensitivity enhancement in ^{2}H NMR. At the same time, it permits selective observation of polymer segments of reduced dynamics, e.g. due to interactions with a surface.

High-resolution ^{13}C NMR of fluoropolymers. Through combination of fast magic-angle spinning and pulsed ^{19}F decoupling, we have obtained the first high-resolution ^{13}C NMR spectra of perfluorinated polymers, such as Teflon and Nafion, an important proton-exchange membrane used in fuel cells.

Two-dimensional NMR of clay-polymer nanocomposites. We have introduced new two-dimensional heteronuclear NMR methods with ^{1}H spin diffusion for characterizing the chemical nature and dynamics of polymer segments 0.3 – 30 nm from a clay silicate surface. Through five-fold sensitivity enhancement of ^{29}Si NMR, samples containing only 5% clay can be characterized. These methods are used to guide new one-pot micellization strategies of producing hydrophobic polymers containing exfoliated clay platelets. In block-copolymer/clay composites, we have proved selective clay-intercalation of one polymer block.

Tie-molecule bundles in drawn polyethylene. We have discovered a major intermediate component, neither crystalline nor amorphous, in drawn polyethylene, and characterized its structure and dynamics. Spin diffusion NMR studies strongly suggest that these are 3-nm-diameter tie-molecule bundles, which are responsible for the material's strength.

Program Impact:
Our work provides insights on the microscopic origins of macroscopic properties of heterogeneous polymers; hopefully, this will eventually lead to improved materials. The NMR techniques developed by our group have been and will be used worldwide by other NMR groups.

Interactions:
Iowa State University: Materials Chemistry (S. Mallapragada)
U.S. Universities: Dept. of Polymer Science & Engineering, Univ. of Mass Amherst
Non-U.S. Universities: Dept. of Physics, Univ. of Sao Carlos, Brazil
U.S. National Laboratories: U.S. Army Research Laboratory, Aberdeen Proving Grounds

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
John H. Dillon Medal of the Polymer Division of the American Physical Society (2001)
15 invited talks

Personnel Commitments for FY2002 to Nearest +/- 10%:
K. Schmidt-Rohr (group leader, 20%), S.-S. Hou (90%), Y. Levin (30%), Q. Chen (40%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $293,000 **FY01 BA** $297,000 **FY02 BA** $316,000

Laboratory Name: Ames Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Materials Chemistry

FWP Number: AL-90-360-001

Program Scope: Quasicrystals are atomically-ordered intermetallics which lack periodicity. They also possess a tantalizing combination of physical properties. Many of their properties are atypical in view of their chemical composition, which is typically aluminum-rich. Our basic goal is to understand how and why the distinctive physical properties derive from the distinctive atomic and electronic structure.

Major Program Achievements (over duration of support):
Surface preparation and characterization. We determined that flat, stable surfaces can be produced by sputter-annealing (assuming appropriate annealing temperatures) and that these surface terminations are bulk-like. We have used a multitude of powerful surface techniques to reach this conclusion. Surfaces exposed to atmosphere develop a passivating layer of aluminum-oxide.
Chemical reactivity. Researchers had suggested that quasicrystals are chemically-inert. Our continuing work in this area suggests that this is not true,for the aluminum-based quasicrystals.
New apparatus acquisition. We purchased a combined variable-temperature scanning tunneling microscopy and scanning Auger microscopy apparatus, and used it to initiate studies of metallic film growth on quasicrystalline substrates.
New and ongoing collaborations. We have initiated external collaborations with numerous groups in the areas of phonon dispersion, porosity determination, quantitative surface composition analysis, interfacial chemistry and bulk structure. Ongoing collaborations continue. (see Interactions).
Other major accomplishments regarding crystal growth, and discovery of new phases, are found elsewhere in Ames Lab materials.

Program Impact:
Our work has motivated and facilitated a number of new research projects around the world. This is indicated by the rates of our manuscript citations and invited talks. Our work has altered the way researchers think about surfaces of quasicrystalline.

Interactions:
Iowa State University: Materials Chemistry (V. Sheares, G. Miller); Condensed Matter Physics (D. Lynch, C. Swenson); Metallurgy & Ceramics (W. McCallum, B. Cook, S. Biner, D. Rehbein, I. Anderson)
U.S. Universities: Carnegie-Mellon Univ,; Pennsylvania State Univ.
Non-U.S. Universities: ETH Hönggerberg; ETH Zurich; Osaka Univ.; Technion Univ.; Université Pierre et Marie Curie; Univ. Liverpool; Univ. Newcastle; Univ. New South Wales; Univ. Nijmegen; Univ. Rostock.
U.S. National Laboratories: ANL; BNL; INEEL; LBNL, SNL

Non-U.S. Laboratories: CNRS, France; Institut für Festkörperforschung, Germany; NIMS, Japan
Industrial: Engineered Coatings, Inc.; Spire Corporation

Recognitions, Honors and Awards (partly attributable to support under this FWP or subtask):

Fellow, both of the American Vacuum Society and the American Physical Society (2000)
Invited presentations: 8

Personnel Commitments for FY2002 to Nearest +/- 10%:
P. Thiel (Group Leader, 10%), T. Lograsso (10%), C. Jenks (30%), M. Kramer (10%), D. Sordelet (50%), J. Anderegg (20%), M. Besser (60%), A. Ross (50%), M. Avila (100%), M. Lemieux (20%), C. Dong (40%), J. Barrow (50%), J. Bjergaard (40%), T. Cai (10%), K. Swainston (40%), Haaland (70%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $764,400 **FY01 BA $**704,300 **FY02 BA $**696,100